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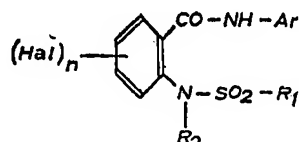
COMPLETE SPECIFICATION

Process for the production of new Aminobenzoic Acid Derivatives and their use in Pest Control

We, J. R. GEIGY A.-G. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns processes for the production of new derivatives of anthranilic acid, as well as agents for combatting injurious insects which contain these compounds as active ingredients; the invention also concerns the use of the new compounds for combatting injurious insects, in particular for the protection of keratine material from these insects, and the keratine material itself thus protected. The invention also concerns the new anthranilic acid derivatives produced according to the process of the invention.

It has surprisingly been found that N-sulphonylated anthranilic acid arylamides of the general formula



wherein Ar represents a phenyl, phenoxyphenyl or phenylmercaptophenyl radical substituted by halogen and/or trifluoromethyl, in particular a chlorinated phenyl, phenoxyphenyl or phenylmercaptophenyl radical, which radical may also possibly be substituted by methyl or alkoxy groups having 1 to 4 carbon atoms,

R₁ represents an alkyl radical having 1 to 4 carbon atoms,

R₂ represents hydrogen or an alkyl radical having 1 to 4 carbon atoms,

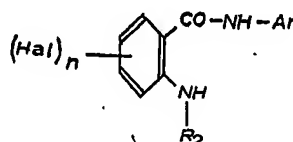
Hal represents chlorine or bromine, and n represents a whole number from 1 to 4, and the total number of halogen atoms and

[Price 3s. 6d.]

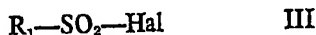
trifluoromethyl groups present as ring substituents in the molecule is greater than two, have excellent insecticidal activity in particular against insects in all their stages of development which are injurious to keratine material such as moth larvae, black carpet beetle and furniture carpet beetle larvae.

The halogen preferred in the benzoic acid radical and in the radical Ar as substituent is chlorine. Generally the radical Ar always contains at least one halogen atom, in particular a chlorine atom, and in addition it can advantageously contain one or more trifluoromethyl radicals. It is also possible however, in order to obtain valuable active ingredients against insects injurious to keratine material, for the radical Ar to contain only trifluoromethyl radicals as substituents as, for the attainment of an insecticidal action, halogen and trifluoromethyl groups are equivalent and the one can be exchanged for the other. If the radical Ar is a phenyl radical which contains a methyl or low alkoxy group as substituent in addition to halogen and/or trifluoromethyl, then this methyl or alkoxy group should advantageously be in the o-position to the coupling position with the —NH— group. If the radical Ar is a substituted phenoxyphenyl or phenylmercaptophenyl radical, then the preferred active compounds are those in which both phenyl radicals are halogenated or trifluoromethylated and the coupling position with the —NH— group is in o-position to the oxygen or sulphur atom binding the nuclei.

The new compounds of the formula I defined above can be produced by reacting an anthranilic acid arylamide of the general formula

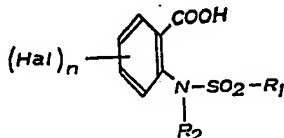


with an alkyl sulphonyl halide of the general formula



wherein R_1 , R_2 , Ar, Hal and n have the meanings given above. The reaction components are so chosen that in all at least three halogen atoms and/or CF_3 groups are contained as ring substituents in the reaction product.

A further process for the production of compounds of the general formula I consists in reacting a halide anhydride or ester of a sulphonyl anthranilic acid of the general formula

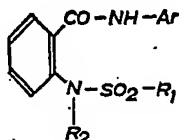


with an amine of the general formula



in the presence of an acid binding agent, R_1 , R_2 , Ar, Hal and n having the meanings given above. The reaction components are so chosen that in all at least three halogen atoms and/or CF_3 groups are contained as ring substituents in the reaction product.

In general those reaction components of the general formulae II-V are chosen as starting materials which produce reaction products having in all at least three halogen atoms and/or CF_3 groups as substituents. However, also pairs of starting materials can be used which contain no, or together contain less than three halogen atoms or CF_3 groups as substituents. The reaction products obtained which correspond to the general formula



wherein the symbols Ar, R_1 and R_2 have the meanings given above but in which in the ring and/or in the radical Ar no or in all less than three halogen atoms and/or CF_3 groups are present, are then treated with chlorine or bromine until as many chlorine or bromine atoms have entered the molecule as ring substituents that the total number of halogen atoms and CF_3 groups in the end product is greater than 2. If desired, reaction products already having the necessary amount of at least 3 halogen atoms and CF_3 groups can also be further treated with chlorine or bromine in order to increase the halogen content.

If desired, the reaction products obtained by one of the above processes in which R_2 is hydrogen can be reacted in the presence of acid binding agents or after conversion into an alkali metal salt, with an alkyl halide or sulphate having 1 to 4 carbon atoms in order to convert the radical R_2 into an alkyl radical.

Starting materials of the general formula II for the first production process are obtained for example from possibly halogen substituted o-nitrobenzoic acids by converting them into their acid chlorides, reacting the latter with arylamines of the general formula V which are possibly substituted in the nucleus, to form the corresponding o-nitrobenzoic acid arylamides, and reducing these to the corresponding anthranilic acid arylamides. If desired these can also be chlorinated or brominated in the nuclei.

The processes for obtaining starting materials of the general formula IV for the second production process depend to some extent on the position of the halogen substituents in relation to the amino group of the anthranilic acid. Unsubstituted anthranilic acid and some nuclear halogenated and/or N-monoalkylated anthranilic acids can be acylated by reaction with acid halides of sulphonic acids of the general formula III, whereupon the N-acyl derivatives of anthranilic acid, possibly after nuclear halogenation, are converted into reactive functional derivatives with regard to the carboxyl group, e.g. into acid halides.

It is very difficult to N-acylate halogen anthranilic acids having a halogen atom in the o-position to the amino group such as 3,5-dichloranthranilic acid. On the other hand, halogenated anthranilic acids as well as anthranilic acid itself and N-monoalkylated derivatives thereof can be converted by treatment with phosgene into possibly nuclear halogenated and/or N-alkylated isatoic acid anhydrides and these can be reacted with arylamines of the general formula V to form starting materials of the general formula II for the first production process. The substances so obtained can then, if desired, be halogenated in the nucleus. The isatoic acid anhydrides necessary for this can be obtained for example also by reacting possibly nuclear halogenated phthalic acid monoamides or imides according to Hoffmann, i.e. isatoic acid anhydrides which are obtained all the same from phthalic acid derivatives but in one instead of two steps, so avoiding the treatment with phosgene.

Examples of suitable starting materials of the general formula II which possibly may also not be halogenated are the arylamides defined of anthranilic acid, 4-chloranthranilic acid, 5-chloranthranilic acid, 3,5-dichloranthranilic acid, 4,5-dichloranthranilic acid, 4,6-dichloranthranilic acid, 3,4,5-trichloranthranilic acid and 3,4,5,6-tetrachloranthranilic acid, 5-bromanthranilic acid, 3,5-dibromanthranilic acid, N-methyl-4,5-dichlor-

anthranilic acid, N-ethyl-4.5-dichloranthranilic acid, N-methyl- and N-ethyl-3.5-dichloranthranilic acid, N-methyl- and N-ethyl-4-chloranthranilic acid and N-methyl-4.6-dichloranthranilic acid.

The amine components in these amides can be represented for example by the following amines of general formula V: aniline, 2-chlor-, 3-chlor- and 4-chlor-aniline, 3.4-dichloraniline and other dichloranilines, 2.4.5-trichloraniline, 3.4.5-trichloraniline, 2.3.4.5-tetrachloraniline, 3-chloro-4-bromaniline, 3.4-dibromaniline, 3-trifluoromethyl-4-chloraniline, 2-chloro-5-trifluoromethyl aniline, 2.5-dichloro-4-trifluoromethyl aniline, 2-methoxy-3.4.5-trichloraniline, 2-methyl-4.5-dichloraniline, mono- and polychlorinated 2-, 3- and 4-amino-diphenyl ether and 4-amino diphenyl sulphides such as, e.g. 2-amino-4.4'-dichlorodiphenyl ether, 3-amino-4.4'-dichlorodiphenyl ether, 2-amino-4.2'.4'.5'.5'-tetrachlorodiphenyl ether and 2-amino-4.5.2'.4'.6'.pentachlorodiphenyl ether as well as 2-amino-4.4'-dichlorodiphenyl sulphide.

Examples of reactive functional derivatives of sulphonic acids of the general formula III are methane sulphonylchloride, ethane sulphonylchloride and butane sulphonylchloride.

Starting materials of the general formula IV are for example the chlorides of anthranilic acids substituted at the nitrogen atom by the radical of a previously named sulphonylchloride. Examples of anthranilic acids from which such N-sulphonyl derivatives are derived have been given above as acid components of amides of the general formula II. Arylamines of the general formula V suitable as starting materials have already been listed as amine components of amides of the general formula II.

Starting materials of the general formula VI for the third production process mentioned are obtained by reacting together pairs of starting materials of the general formulae II and III or IV and V, in both of which pairs there are no or only few chlorine atoms as substituents.

The following examples illustrate the production of the new compounds. Parts are given as parts by weight and their relationship to parts by volume is as that of grammes to cubic centimetres. The temperatures are in degrees Centigrade.

EXAMPLE 1

a) 2-Methane sulphonamido-5-chlorobenzoic acid

171.5 Parts of 5-chloranthranilic acid are suspended in 2000 parts of water and 500 parts of 40% caustic soda lye are added. The solution is heated to about 60° until the chloranthranilic acid has completely dissolved and then it is cooled to 10°. 170 Parts of methane sulphonylchloride are added dropwise at this temperature. The temperature of the reaction mixture is then allowed to rise to about 20° and it is stirred for some hours at this temperature. The 2-methane sulphon-

amido-5-chlorobenzoic acid is then precipitated with concentrated hydrochloric acid. It is filtered off, washed neutral with water and dried at 100° in the vacuum.

The crude product obtained in this way melts at about 185—190°. It can be recrystallised from methanol and water. The pure compound melts at 200—202°.

b) 2-Methane sulphonamido-5-chlorobenzoyl chloride

249.5 Parts of 2-methane sulphonamido-5-chlorobenzoic acid are suspended in 1000 parts by volume of benzene and 300 parts of phosphorus pentachloride are added at about 40—50°. A complete solution is obtained. As soon as no more hydrochloric acid gas is developed, the mixture is cooled to about 10° whereupon the 2-methane sulphonamido-5-chlorobenzoyl chloride practically completely crystallises out. It is filtered off and washed with petroleum ether. It is dried in the vacuum at about 50° and melts at 131—133°.

c) 2-Methane sulphonamido-5-chlorobenzoic acid-2'.3'.4'.5'.5'-tetrachloranilide

268 Parts of 2-methane sulphonamido-5-chlorobenzoyl chloride are dissolved in 2000 parts of benzene and a solution of 462 parts of 2.3.4.5-tetrachloraniline in 1000 parts of benzene is added at room temperature. The mixture is heated at 60° while stirring for 30 minutes and then cooled to room temperature. The product can be worked up as follows: 250 ccm of 40% caustic soda lye are added dropwise while cooling and the reaction product precipitates from the reaction mixture as the sodium salt. The precipitate is filtered off and dissolved hot in about 3000 parts of water. The solution is clarified with active charcoal and filtered. The product is precipitated from the filtrate by acidifying with concentrated hydrochloric acid. It is washed neutral with water and dried in the vacuum at 80°.

The crude compound melts at about 230—235°. On recrystallising from 2-methoxyethanol it is obtained in a pure state and then melts at 240—242°.

EXAMPLE 2

a) Anthranilic acid-3.4-dichloranilide

162 Parts of 3.4-dichloraniline are dissolved in 1000 parts by volume of chlorobenzene. The solution is heated to 60° and at this temperature a solution of 190 parts of o-nitrobenzoyl chloride in 500 parts of chlorobenzene is added dropwise. The reaction mixture is then refluxed until no more hydrochloric acid gas is developed (about 15—20 hours). On cooling, the o-nitrobenzoic acid dichloranilide practically completely precipitates out. It is filtered and dried in the vacuum at 100°. The crude compound melts at 170—175°. The pure product, recrystallised from butanone, melts at 179—181°.

The crude nitro compound obtained in this way can be reduced in the usual manner

according to Béchamp, i.e. with iron and acetic or hydrochloric acid.

After recrystallisation from chlorobenzene, the anthranilic acid-3.4-dichloranilide melts at 142—143°.

b) 2-Amino-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide

The anthranilic acid dichloranilide is chlorinated as follows:

281 Parts of anthranilic acid dichloranilide are dissolved in 2000 parts of glacial acetic acid and 142 parts of chlorine are introduced slowly at a temperature which does not exceed 40°. A thick paste is obtained which consists of the hydrochloride of 2-amino-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide. It is filtered under suction and dried at 80° in the vacuum. The hydrochloride can be used direct for the following step. If the free amine is produced by treating the hydrochloric acid salt with caustic soda lye, the crude amine melts at about 185—190°. The pure 2-amino-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide (after recrystallisation from 2-ethoxyethanol) melts at 205—206°.

c) 2-Methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide

350 Parts of 2-amino-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide are dissolved in 2000 parts of dioxan or a similar solvent and, at 30—40°, 10% caustic soda lye and a solution of 170 parts of methane sulphochloride in 500 parts of dioxan are added dropwise simultaneously in such a manner that the solution always remains alkaline.

The product is worked up by removing the dioxan by the introduction of steam and diluting the alkaline residue with 5000 parts of water. The solution can be further clarified with active charcoal and filtered. On acidifying with concentrated hydrochloric acid the 2-methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide is precipitated. It is filtered off, washed neutral with water and dried in the vacuum at about 100°. The crude product melts at about 235—240°.

It can be obtained in a pure state by recrystallising from chlorobenzene whereupon it melts at 248—249°.

d) N-methyl-methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide

428 Parts of 2-methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide are suspended in 3500 parts of water and the reaction is made alkaline with about 100 parts of concentrated (40%) caustic soda lye. The mixture is then heated to about 50° and 300 parts of dimethyl sulphate are added. The mixture is kept continually phenolphthalein alkaline by the slow addition of concentrated caustic soda lye. The reaction product is completely precipitated after some hours. It is filtered off, washed neutral with water and dried in the vacuum at about 100°.

The crude 2-methane sulphone methyl-

amido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide produced in this manner melts at about 190—195°. The pure compound can be obtained by recrystallisation from alcohol or benzene. It melts at 204—205°.

EXAMPLE 3

a) 3.5-Dichlorisatoic acid anhydride

206 Parts of 3.5-dichloranthranilic acid are suspended in 1500 parts by volume of chlorobenzene. 150 Parts of phosgene are introduced into this suspension at 120°. The reaction mixture is then refluxed for some hours and finally cooled to room temperature. The greater part of the 3.5-dichlorisatoic acid anhydride crystallises out of the chlorobenzene solution and can be filtered off. After drying in the vacuum at about 100° it decomposes at about 250°. A further amount of less pure product can be obtained by concentrating the mother lye.

b) 2-Amino-3.5-dichlorobenzoic acid-3¹.4¹.5¹-trichloranilide

232 Parts of 3.5-dichlorisatoic acid anhydride are added at 100° to a solution of 105 parts of 3.4.5-trichloraniline in 2000 parts by volume of chlorobenzene. The reaction mixture is refluxed for 10 hours and then cooled to room temperature whereupon the greater part of the crude 2-amino-3.5-dichlorobenzoic acid-3¹.4¹.5¹-trichloranilide precipitates. It is filtered off and dried in the vacuum at about 100°. The crude product melts at about 205—210°. The pure compound can be obtained by recrystallisation from chlorobenzene. It then melts at 213—215°.

c) 2-Methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹.5¹-trichloranilide

The 2-amino-3.5-dichlorobenzoic acid-3¹.4¹.5¹-trichloranilide is methane sulphonated in exactly the same manner as described in example 2 under c).

The crude product obtained in this way melts at about 292—295°. The pure compound which can be obtained by recrystallisation from 2-ethoxyethanol, melts at 297—298°.

EXAMPLE 4

Production of 2-methane sulphonamido-5-chlorobenzoic acid-3¹.4¹-dichloranilide by chlorination of 2-methane sulphonamido benzoic acid-3.4-dichloranilide

359 Parts of 2-methane sulphonamido benzoic acid-3.4-dichloranilide (M.P. 198—199°) are suspended in 2000 parts of glacial acetic acid and 75 parts of chlorine are introduced at 40—45°. The halogen is easily taken up so that the chlorination can be performed fairly quickly.

The reaction mixture is diluted with water and the chlorination product which precipitates in crystalline form is filtered off under suction and washed with water. After drying in the vacuum at about 100°, it melts at 195—199°. The pure compound can be obtained by

recrystallisation from 2-ethoxyethanol. It melts at 201—203°.

- The melting point of the product mixed with the starting material is strongly depressed. Analysis shows that the compound contains three chlorine atoms and it can be shown by break-down reactions that halogen substitution has occurred in the 5-position of the anthranilic acid derivative.

EXAMPLE 5

- a) N-Methyl-4.5-dichlorisatoic acid anhydride
220 Parts of N-methyl-4.5-dichloranthranilic acid are dissolved in 2000 parts by volume of chlorobenzene. 150 Parts of phosgene are slowly introduced at 120° and then the reaction mixture is refluxed until the hydrochloric acid development is complete (about 5 hours). On cooling, the greater part of the N-methyl-4.5-dichlorisatoic acid anhydride crystallises out. It is filtered off and washed with chlorobenzene and with petroleum ether. After drying at about 100° in the vacuum it melts at 196—198°.

- b) N-Methyl-4.5-dichloranthranilic acid-3¹.4¹-dichloranilide

- 244 Parts of N-methyl-4.5-dichlorisatoic acid anhydride and 162 parts of 3.4-dichloraniline in 1500 parts of chlorobenzene are refluxed. The CO₂ development is completed after about 2 hours. The reaction mixture is then cooled to room temperature whereupon the greater part of the reaction product precipitates. It is filtered off and washed first with chlorobenzene and then with petroleum ether. After drying in the vacuum at about 100°, the crude N-methyl-4.5-dichloranthranilic acid-3¹.4¹-dichloranilide melts at about 250—255°. It can be recrystallised from 2-ethoxyethanol and then melts at 257—258°.

- c) 2-(N-methyl-methane sulphonamido)-4.5-dichlorobenzoic acid-3¹.4¹-dichloranilide

- 364 Parts of N-methyl-4.5-dichloranthranilic acid-3¹.4¹-dichloranilide are dissolved with 1000 parts of dioxan and 500 parts of 20% caustic soda lye. 170 Parts of methane sulphonylchloride are then slowly added dropwise at 40—50°. The reaction mixture is then stirred for 1 hour at about 40° and then cooled to room temperature. On acidifying with concentrated hydrochloric acid the greater part of the reaction product precipitates and can be filtered off. It is washed first with a little dioxan and then with water until the reaction is neutral. After drying at about 100° in the vacuum, the crude product melts at about 180—185°. After recrystallisation from chlorobenzene, the pure compound melts at 185—186°.

- The following compounds for example can be produced in an analogous manner to those described in the above examples; all melting points are given in degrees Centigrade.

- 2 - methane sulphonamido - 5 - chlorobenzoic acid - 3¹ - chloro - 4¹ - bromanilide
M.P. 211—213°, 2 - methane sulphonamido-

5 - chlorobenzoic acid - 3¹.4¹.5¹ - trichloranilide M.P. 240—242°, 2 - methane sulphonamido - 5 - chlorobenzoic acid - 2¹.4¹ - dichloro - 5¹ - trifluoromethyl anilide M.P. 195—198°, 2 - methane sulphonamido - 5-chlorobenzoic acid - 2¹.4¹.5¹ - trichloranilide M.P. 198—200°, 2 - methane sulphonamido-4 - chlorobenzoic acid - 3¹.4¹ - dichloranilide M. P. 255—257°, 2 - methane sulphonamido-3.5 - dichlorobenzoic acid - 2¹ - methoxy-3¹.4¹.5¹ - trichloranilide M.P. 240—241°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹.3¹.4¹.5¹ - tetrachloranilide M.P. 280—282°, 2 - methane sulphonamido-3.5 - dichlorobenzoic acid - 4¹ - chloranilide M.P. 270—271°, 2 - methane sulphonamido-3.5 - dichlorobenzoic acid - 3¹ - chloro - 4¹ - bromanilide M.P. 268—269.5°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid-2¹.4¹.5¹ - trichloranilide M.P. 274—275°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 3¹ - trifluoromethyl - 4¹ - chloranilide M.P. 237—238°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹ - (4¹¹-chlorophenoxy) - 5¹ - chloranilide M.P. 206—207°, 2 - (N - methyl - methane sulphonamido) - 3.5 - dichlorobenzoic acid-2¹.4¹.5¹ - trichloranilide M.P. 150—151°, 2 - (N - methyl - methane sulphonamido)-3.5 - dichlorobenzoic acid - 2¹ - (4¹¹ - chlorophenoxy) - 5¹ - chloranilide M.P. 173—175°, 2 - (N - methyl - methane sulphonamido)-3.5 - dichlorobenzoic acid - 3¹.4¹ - dichloranilide M.P. 143—144°, 2 - (N - isopropyl-methane sulphonamido) - 3.5 - dichlorobenzoic acid - 3¹.4¹ - dichloranilide M.P. 150—151°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹ - (2¹¹.4¹¹.5¹¹ - trichlorophenoxy) - 5¹ - chloranilide M.P. 210—212°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹ - (2¹¹.4¹¹.6¹¹ - trichlorophenoxy) - 4¹.5¹ - dichloranilide M.P. 247—249°, 2 - methane sulphonamido - 3.5-dichlorobenzoic acid - 2¹ - (4¹¹ - chlorophenylmercapto) - 5¹ - chloranilide M.P. 236—238°, 2 - methane sulphonamido - 4.5-dichlorobenzoic acid - 3¹.4¹ - dichloranilide M.P. 228—230°, 2 - Methane sulphonamido-4.5 - dichlorobenzoic acid - 2¹.4¹.5¹ - trichloranilide M.P. 178—180°, 2 - methane sulphonamido - 4.5 - dichlorobenzoic acid - 3¹.4¹.5¹-trichloranilide M.P. 271—272°, 2 - ethane sulphonamido - 3.5 - dichlorobenzoic acid-3¹.4¹ - dichloranilide M.P. 257—258°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹ - methyl - 4¹.5¹ - dichloranilide M.P. 216—218°, 2 - (N - n - butyl-methane sulphonamido) - 3.5 - dichlorobenzoic acid - 3¹.4¹ - dichloranilide M.P. 169—171°, 2 - methane sulphonamido - 3.5 - dichlorobenzoic acid - 2¹ - chloro - 5¹ - trifluoromethyl anilide M.P. 268—270°, 2 - n - butane sulphonamido - 3.5 - dichlorobenzoic acid-3¹.4¹ - dichloranilide M.P. 224—226°, 2 - methane sulphonamido - 3.4.5 - trichloro-

benzoic acid - 3¹.4¹ - dichloranilide M.P. 267—269°, 2 - methane sulphonamido - 5-bromobenzoic acid - 3¹.4¹ - dichloranilide M.P. 195—197°, 2 - methane sulphonamido-3.5 - dibromobenzoic acid - 3¹.4¹ - dichloranilide M.P. 238—240°.

The compounds of formula I which can be produced according to the processes described can be used according to the usual methods for textile finishing. They have considerable affinity to keratine material and are excellently suitable therefore, for the protection of keratine material against injurious insects, in particular for the wash and moth proof finishing of such materials both in the raw as well as in the processed state, for example of raw or processed sheep's wool as well as other animal hairs, fells and furs. In addition to the wash and moth proof finishing in the dyebath, the compounds can also be used for the impregnation of wool or woollen articles the materials then becoming equally excellently moth proofed.

In addition to their insecticidal action on the larvae of the clothes moth, the compounds of formula I are also active against the larvae of the black carpet and furniture carpet beetles so that the textiles, such as woollen blankets, woollen carpets, woollen underwear, woollen clothes and knitted goods treated with the compounds according to the present invention by one or the other of these methods, are protected from all types of insects which are injurious to keratine material.

The agents used for the protection of keratine material against attack by injurious insects should contain the active ingredients of the formula I in a finely distributed form. Thus, solutions, suspensions and emulsions of the active ingredients should be used.

Insofar as the active ingredients contain a hydrogen atom in the sulphonamide group, i.e. when R₂ is a hydrogen atom, in the form of their alkali metal salts they have good water solubility. They can be applied to the keratine material direct from these aqueous solutions either by dipping the material for a shorter or longer time in the alkali metal salt solutions, or spraying them with the solutions, or by treating them in the solutions at a raised temperature as in dyeing processes.

Compounds having no dissociating hydrogen atom in the sulphonamide group can be drawn onto the material to be protected for example from their aqueous suspensions or emulsions, advantageously at a raised temperature, or such suspensions or emulsions can be used for spraying the material.

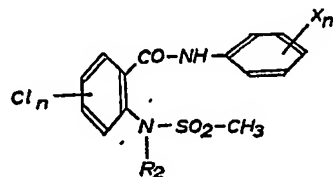
Because of their improved solubility in organic solvents, these compounds are particularly well suited for application from non-aqueous media. Thus the materials to be protected can simply be impregnated with those solutions or, if a suitable solvent is chosen, the moth proof finishing can be combined with

a dry cleaning process.

Propylene glycol, 2-methoxyethanol, 2-ethoxyethanol and dimethyl formamide have proved to be particularly suitable organic solvents to which distributing agents and/or other auxiliaries can be added. Emulsifying agents such as, e.g. sulphonated castor oil, sulphite waste liquor and fatty alcohol sulphonates can be mentioned in particular as distributing agents.

Thus various carriers (such as solvents) and distributing agents are suitable for the application of the active ingredients to the keratine material, depending on the medium and physical state from which the finely distributed active ingredient is applied.

Active ingredients of the formula



in which R₂ is hydrogen or a low alkyl radical, n is a number from 1 to 4, each X is a halogen atom or a CF₃ group, m is a number from 1 to 4 and the sum of m+n is greater than 2 and advantageously at least 4, proved particularly suitable for use in agents for the protection of keratine materials.

EXAMPLE 6

0.5 Parts of 2-methane sulphonamido-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide are dissolved with the aid of 10 parts of 0.1 N-caustic soda lye and a little alcohol. This solution is diluted with 3000 parts of water and 100 parts of wool are treated in the liquor so prepared for 15 minutes at about 60°. 5 Parts of 10% acetic acid are then added and the treatment is continued at 60° for a further hour.

The wool is then tested and dried in the usual way. It is resistant to attack by the larvae of the moth, and of the black carpet and furniture carpet beetles.

EXAMPLE 7

2-(N-methyl-methane sulphonamido)-3.5-dichlorobenzoic acid-3¹.4¹-dichloranilide can be applied, for example, in the following manner:

0.5 Parts of active ingredient are dissolved in 10 parts of dimethyl formamide and the solution is poured into 3000 parts of water which contains about 1—2 parts of an emulsifier, e.g. sulphonated castor oil.

100 Parts of wool are treated for 30 minutes in this liquor at boiling temperature. After rinsing and drying, the wool is moth proof.

Naturally, other additives as well as dye-stuffs can be added to the treatment baths described in examples 6 and 7.

EXAMPLE 8

First a 20% solution of 2-(N-isopropylmethane sulphonamido)-3,5-dichlorobenzoic acid-3',4'-dichloranilide in glycol monoethyl ether is prepared. 10 Parts by volume of this solution are diluted with 200 parts by volume of a solvent suitable for dry cleaning, for example a suitable benzene fraction ("Diluan S"). If desired, other additives having a cleansing action can be added. The woollen articles are then treated in this cleaning liquid in the usual way and then centrifuged to a solvent content of about 100% of the weight of the wool. After drying, they are moth proof.

In an analogous manner, the same or analogously composed baths can also be used for the moth proof finishing of untreated or of already otherwise treated or cleaned articles.

Also similar mixtures can be used for spraying of wool in all stages of processing.

The resistance to attack by injurious insects of the keratinous textile materials treated with the compounds according to the present invention was tested by the following standard methods:

Moths:

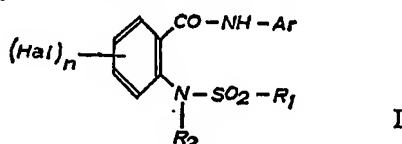
SNV-Normenblatt No. 95901

Furniture carpet beetle (*Anthrenus*):
SNV-Normenblatt No. 95902

Black carpet beetle (*Attagenus*):
AATCC Year Book 1952 p.123 and ff.

WHAT WE CLAIM IS:—

1. N-sulphonated anthranilic acid arylamides of the general formula



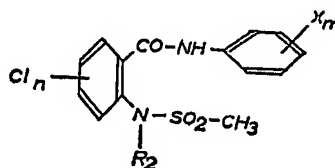
wherein Ar represents a phenyl, phenoxyphenyl or phenylmercaptophenyl radical, which radical is substituted by at least one halogen and/or trifluoromethyl group, especially by chlorine, and which may further be substituted by a methyl or alkoxy group having 1 to 4 carbon atoms,

R₁ is an alkyl radical having 1 to 4 carbon atoms,

R₂ represents hydrogen or an alkyl radical having 1 to 4 carbon atoms,

Hal represents chlorine or bromine, n is a whole number from 1 to 4, and wherein the total sum of halogen atoms and trifluoromethyl groups present in the molecule as substituents on the aromatic rings is greater than 2 and preferably at least 4.

2. N-sulphonated anthranilic acid arylamides of the general formula



wherein R₂ represents hydrogen or an alkyl radical having 1 to 4 carbon atoms,

n is a whole number from 1 to 4,

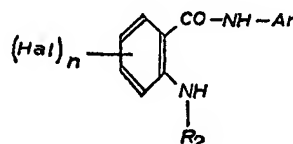
X independently in each occurrence represents chlorine, bromine or a trifluoromethyl group,

m is a whole number from 1 to 4, and the total sum of m + n is greater than 2.

3. The compound 2-methane sulphonamido-3,5-dichlorobenzoic acid-3',4'-dichloranilide.

4. The compound 2-methane sulphonamido-3,5-dichlorobenzoic acid-3',4',5-trichloranilide.

5. A process for the production of N-sulphonated anthranilic acid arylamides of the general formula I given in claim 1, which comprises reacting an anthranilic acid arylamide of the general formula

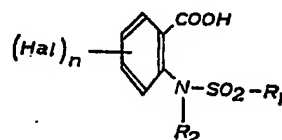


with an alkyl sulphonyl halide of the formula



wherein R₁, R₂, Hal, Ar and n have the meanings given in claim 1, the reaction components being so chosen that the reaction product obtained contains at least 3 halogen atoms and/or trifluoromethyl groups in the rings of its molecule and if desired, treating a resultant reaction product in which R₂ is hydrogen, either in the presence of an acid binding agent or after conversion into an alkali metal salt with an alkyl halide or sulphate having from 1 to 4 carbon atoms.

6. A process for the production of N-sulphonated anthranilic acid arylamides of the general formula I given in claim 1 which comprises reacting in the presence of an acid binding agent a halide anhydride or ester, of an N-sulphonyl anthranilic acid of the general formula

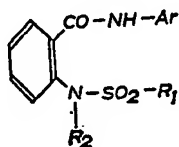


with an arylamine of the general formula



wherein R_1 , R_2 , Hal, Ar and n have the meanings given in claim 1, the reaction components being so chosen that the reaction product obtained contains at least 3 halogen atoms and/or trifluoromethyl groups in the rings of its molecule, and if desired, treating a resultant reaction product in which R_2 is hydrogen, either in the presence of an acid binding agent or after conversion into an alkali metal salt, with an alkyl halide or sulphate having from 1 to 4 carbon atoms.

7. A process which comprises treating an N-sulphonated anthranilic acid of the general formula

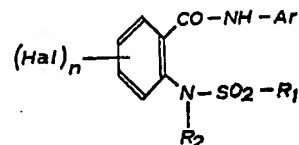


in which Ar, R_1 and R_2 have the meanings defined in claim 1, and which may contain no or less than 3 halogen atoms and/or trifluoromethyl groups in the molecule, with chlorine or bromine until so many chlorine or bromine atoms have entered at least one of the aromatic rings of the molecule that the total sum of halogen atoms and CF_3 groups in the molecule reaches at least 3.

8. A process as claimed in claim 7 in which the reaction product in which R_2 is hydrogen is treated either in the presence of an acid binding agent or after conversion to an alkali metal salt, with an alkyl halide or sulphate having from 1 to 4 carbon atoms.

9. A process for the protection of keratine

material from injurious insects which comprises the treatment of the material with compositions comprising compounds of the general formula



wherein R_1 , R_2 , Ar and n have the meanings given in claim 1, together with a surface active agent and a carrier.

10. The keratine material protected from injurious insects by the use of compounds of the general formula I given in claim 1.

11. A composition of matter containing an N-sulphonated anthranilic acid arylamide of the general formula I given in claim 1 together with a carrier, and if desired a surface active agent.

12. A composition of matter as claimed in claim 11 in the form of a solution, emulsion or suspension.

13. A process for the production of N-sulphonated anthranilic acid arylamides of the general formula I defined in claim 1 substantially as hereinbefore described in any one of the examples.

14. N-sulphonated anthranilic acid arylamides claimed in claim 1 as hereinbefore described in any one of the examples.

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